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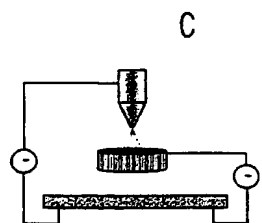
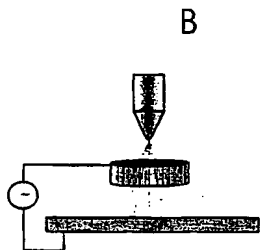
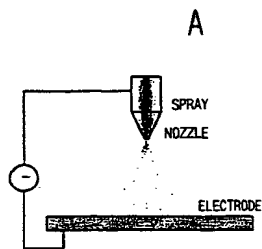
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(54) Title: A HYBRID POLYMER ELECTROLYTE FABRICATED BY A SPRAY METHOD, A LITHIUM SECONDARY BATTERY COMPRISING THE HYBRID POLYMER ELECTROLYTE AND THEIR FABRICATION METHODS



(57) Abstract: The present invention provides a novel hybrid polymer electrolyte, a lithium secondary battery comprising the hybrid polymer electrolyte and their fabrication methods. More particularly, the present invention provides the hybrid polymer electrolyte comprising a porous polymer matrix with particles, fibers or mixture thereof having diameters of 1 - 3000 nm, polymers and lithium salt-dissolved organic electrolyte solutions incorporated into the porous polymer matrix. The hybrid polymer electrolyte has advantages of better adhesion with electrodes, good mechanical strength, better performance at low- and high-temperatures, better compatibility with organic electrolytes of a lithium secondary battery and it can be applied to the manufacture of lithium secondary batteries.

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A HYBRID POLYMER ELECTROLYTE FABRICATED BY A SPRAY METHOD, A LITHIUM SECONDARY BATTERY COMPRISING THE HYBRID POLYMER ELECTROLYTE AND THEIR FABRICATION METHODS

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TECHNICAL FIELD

The present invention relates to a hybrid polymer electrolyte fabricated by a spray method, a lithium secondary battery using the same and its fabrication method.

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BACKGROUND ART

Lithium secondary batteries are typified by a lithium ion battery and a lithium polymer battery. A lithium ion battery uses a polyethylene (hereinafter referred to as "PE") or polypropylene (hereinafter referred to as "PP") separator film besides an electrolyte. Because it is difficult to fabricate the lithium ion battery by laminating electrodes and separator films in a flat-plate shape, it is fabricated by rolling the electrodes with separator films and by inserting them into a cylindrical or rectangular casing (D. Linden, *Handbook of Batteries*, McGraw-Hill Inc., New York (1995)). The lithium ion battery was developed by SONY Company in Japan and has been widely used all over the world; however, it has problems such as instability of the battery, intricacy of its fabrication process, restriction on battery shape and limitation of capacity.

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On the contrary, a lithium polymer battery uses a polymer electrolyte

having two functions, as a separator film and as an electrolyte at the same time, and it is now being viewed with keen interest as a battery being able to solve all of the problems. The lithium polymer battery has an advantage in view of productivity because the electrodes and a polymer electrolyte can be
5 laminated in a flat-plate shape and its fabrication process is similar to a fabrication process of a polymer film.

A conventional polymer electrolyte is mainly prepared with polyethylene oxide (hereinafter referred to as "PEO"), but its ionic conductivity is merely 10^{-8} S/cm at room temperature, and accordingly it can not be used
10 commonly.

Recently, a gel or hybrid type polymer electrolyte having an ionic conductivity above 10^{-3} S/cm at room temperature has been developed.

K. M. Abraham *et al.* and D. L. Chua *et al.* disclose a polymer electrolyte of a gel type polyacrylonitrile (hereinafter referred to as "PAN")
15 group in U.S. Patent No. 5,219,679 and in U.S. Patent No. 5,240,790 respectively. The gel type PAN group polymer electrolyte is prepared by injecting a solvent compound (hereinafter referred to as an "organic electrolyte solution") prepared with a lithium salt and organic solvents, such as ethylene carbonate and propylene carbonate, etc., into a polymer matrix.
20 It has advantages in that the contact resistance is small in charging/discharging of a battery and desorption of the active materials rarely takes place because the adhesive force of the polymer electrolyte is good, and accordingly adhesion between a composite electrode and a metal substrate is well developed. However, such a polymer electrolyte has a

problem in that its mechanical stability, namely its strength, is low because the electrolyte is a little bit soft. Especially, such deficiency in strength may cause many problems in the fabrication of an electrode and battery.

A. S. Gozdz *et al.* discloses a polymer electrolyte of hybrid type polyvinylidenedifluoride (hereinafter referred to as "PVdF") group in U.S. Patent No. 5,460,904. The polymer electrolyte of the hybrid type PVdF group is prepared by fabricating a polymer matrix having a porosity not greater than submicron and then injecting an organic electrolyte solution into the small pores into the polymer matrix. It has advantages in that its compatibility with the organic electrolyte solution is good, the organic electrolyte solution injected into the small pores is not leaked so as to be safe in use, and the polymer matrix can be prepared in the atmosphere because the organic electrolyte solution is injected later. However, it has disadvantages in that the fabrication process is intricate because in the preparation of polymer electrolyte, an extraction process of a plasticizer and an impregnation process of an organic electrolyte solution are required. In addition, it has a critical disadvantage in that a process for forming a thin layer by heating and an extraction process are required in fabrication of electrodes and batteries because the mechanical strength of the PVdF group electrolyte is good but its adhesive force is poor.

Recently, a polymer electrolyte of a polymethylmethacrylate (hereinafter referred to as "PMMA") group was presented in *Solid State Ionics*, 66, 97, 105 (1993) by O. Bohnke and G. Frand, *et al.* The PMMA polymer electrolyte has advantages in that it has an ionic conductivity of 10^{-3}

S/cm at room temperature, and its adhesive force and compatibility with an organic electrolyte solution are good. However, it is not suitable for lithium polymer batteries because its mechanical strength is very poor.

In addition, a polymer electrolyte of a polyvinylchloride (hereinafter referred to as "PVC") group, which has good mechanical strength and has an ionic conductivity of 10^{-3} S/cm at room temperature, was presented in *J. Electrochem. Soc.*, 140, L96 (1993) by M. Alamgir and K. M. Abraham. However, it has disadvantages in that its low-temperature characteristic is poor and its contact resistance is high.

Accordingly, development of a polymer electrolyte having a good adhesion with electrodes, good mechanical strength, good low- and high-temperature characteristics, and good compatibility with an organic electrolyte solution for a lithium secondary battery, etc. has been required.

15

SUMMARY OF THE INVENTION

It is an object of the present invention to provide a novel hybrid polymer electrolyte.

It is another object of the present invention to provide a hybrid polymer electrolyte having a good adhesion with electrodes, good mechanical strength, good low- and high-temperature characteristics and good compatibility with an organic electrolyte solution for a lithium secondary battery, etc., and its fabrication method.

It is yet another object of the present invention to provide a lithium secondary battery having a simplified fabrication process, advantage in

scaling-up of a battery size, and superiority in energy density, cycle characteristic, low- and high-temperature characteristics, high rate discharge characteristic and stability, and its fabrication method.

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BRIEF DESCRIPTION OF DRAWINGS

Figures 1a to 1c illustrate embodiments of a spray method by an electrostatic induction.

Figures 2a and 2b illustrate the fabrication of a porous polymer matrix using a spraying machine.

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Figures 3a to 3c illustrate process flow for fabricating lithium secondary batteries according to the present invention.

Figure 4 is a graph illustrating charge/discharge characteristics of the lithium secondary batteries of Examples 1-6 and Comparative Examples 1 and 2.

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Figures 5a and 5b are graphs illustrating low- and high-temperature characteristics of the lithium secondary batteries of Example 2 and Comparative Example 2.

Figures 6a and 6b are graphs illustrating high-rate discharge characteristics of the lithium secondary batteries of Example 2 and

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Comparative Example 2.

DETAILED DESCRIPTION OF THE INVENTION

The present invention relates to a hybrid polymer electrolyte comprising a porous polymer matrix in particulate or fibrous form, or a

combination thereof, having a diameter of 1-3000nm and a polymer electrolyte incorporated into the porous polymer matrix. In more particularity, the present invention relates to a hybrid polymer electrolyte obtained by dissolving a polymer in an organic solvent, fabricating a porous polymer matrix in particulate or fibrous form, or a combination thereof, having a diameter of 1-3000nm by a spray method and then injecting a polymer electrolyte solution, in which a polymer, a plasticizer and an organic electrolyte solution are mixed and dissolved with each other, into the pores in the polymer matrix. In the present description, "hybrid polymer electrolyte" means an electrolyte in which a polymer electrolyte is incorporated into a porous polymer matrix. "Polymer electrolyte solution" means a solution in which a polymer, which is incorporated into a porous polymer matrix, is dissolved in a mixture of a plasticizer and an organic electrolyte solution. An "organic electrolyte solution" means a solution in which a lithium salt is dissolved in an organic solvent, which does not affect characteristics of electrodes. And, "polymer electrolyte" generically means an organic electrolyte solution and a polymer incorporated into the porous polymer matrix.

A porous polymer matrix fabricated by a spray method has a form in which particles or fibers, or a combination thereof having a diameter of 1nm - 3000nm are built up three-dimensionally. Due to the small diameter of the particles or fibers, the ratio of surface area to volume and the void ratio are very high compared to those of a conventional electrolyte. Therefore, due to the high void ratio, the content of electrolyte impregnated is large and the

ionic conductivity is increased, and due to the large surface area, the contact area with the electrolyte can be increased and the leakage of electrolyte can be minimized in spite of the high void ratio.

Furthermore, in spite of the fabrication method in the form of particles
5 or fibers, or a combination thereof, because the final product is fabricated in the form of a film directly, the fabrication equipment and processes are simple, and the fabrication time can be shortened. Therefore, the economic efficiency is high, and the fabrication of the film is also easy. In addition, because the particles or fibers, or combination thereof, are built up to form a
10 structure having pores of effective size, closed pores can not be formed structurally, and there is no possibility of closing the pores during the lamination process applied to fabricate batteries. Furthermore, because DBP, which is used in the conventional process of Bellcore Co. for forming pores, is not used, there is no problem of residual DBP.

15 The examples of the polymer used for forming a porous polymer matrix can include polyethylene, polypropylene, cellulose, cellulose acetate, cellulose acetate butylate, cellulose acetate propionate, polyvinylpyrrolidone-vinylacetate, poly[bis(2-(2-methoxyethoxyethoxy))phosphagene], poly-ethyleneimide, polyethyleneoxide, polyethylenesuccinate, polyethylenesulfide,
20 poly(oxymethylene-oligo-oxyethylene), polypropyleneoxide, polyvinylacetate, polyacrylonitrile, poly(acrylonitrile-co-methylacrylate), polymethylmethacrylate, poly(methylmethacrylate-co-ethylacrylate), polyvinylchloride, poly(vinylidene-chloride-co-acrylonitrile), polyvinylidenedifluoride, poly(vinylidenefluoride-co-hexafluoropropylene) or mixtures thereof. However, the polymer is not limited

to the above examples, and any polymer which can be formed into a porous polymer matrix by a spray method is applicable.

Although there is no specific limitation on the thickness of the porous polymer matrix, it is preferable to have a thickness of 1 μm - 100 μm , more preferably 5 μm - 70 μm , and most preferably 10 μm - 50 μm . The diameter of the particles and fibers of the polymer forming a porous polymer matrix is preferably adjusted in the range of 1 nm - 3000 nm, more preferably 10 nm - 1000nm, and most preferably 50 nm - 500 nm.

The polymer incorporated into the porous polymer matrix functions as a polymer electrolyte, and examples of the polymer can include polyethylene, polypropylene, cellulose, cellulose acetate, cellulose acetate butylate, cellulose acetate propionate, polyvinylpyrrolidone-vinylacetate, poly[bis(2-(2-methoxyethoxyethoxy))phosphagene], polyethyleneimide, polyethyleneoxide, polyethylenesuccinate, polyethylenesulfide, poly(oxymethylene-oligo-oxyethylene), polypropyleneoxide, polyvinylacetate, polyacrylonitrile, poly(acrylonitrile-co-methylacrylate), polymethylmethacrylate, poly(methylmethacrylate-co-ethylacrylate), polyvinylchloride, poly(vinylidenechloride-co-acrylonitrile), polyvinylidenedifluoride, poly(vinylidene fluoride-co-hexafluoropropylene), polyethylene glycol diacrylate, polyethylene glycol dimethacrylate or mixtures thereof.

There is no specific limitation on the lithium salt incorporated into the porous polymer matrix. The preferable examples of the lithium salt can include LiPF_6 , LiClO_4 , LiAsF_6 , LiBF_4 and LiCF_3SO_3 , and among them LiPF_6 is more preferable.

Examples of the organic solvent used in the organic electrolyte solution can include ethylene carbonate, propylene carbonate, diethyl carbonate, dimethyl carbonate, ethylmethyl carbonate or mixtures thereof. In order to improve the low-temperature characteristic, an additional solvent, such as
5 methyl acetate, methyl propionate, ethyl acetate, ethyl propionate, butylene carbonate, γ -butyrolactone, 1,2-dimethoxyethane, 1,2-dimethoxyethane, dimethylacetamide, tetrahydrofuran or mixtures thereof, can be added to the above organic solvent.

The hybrid polymer electrolyte of the present invention can further
10 include a filling agent in order to improve the porosity and mechanical strength. Examples of a filling agent can include TiO_2 , BaTiO_3 , Li_2O , LiF , LiOH , Li_3N , BaO , Na_2O , MgO , Li_2CO_3 , LiAlO_2 , SiO_2 , Al_2O_3 , PTFE or mixtures thereof. It is preferable that the content of the filling agent is generally below 20% by weight of the total hybrid polymer electrolyte.

15 The present invention also relates to a fabrication method for a hybrid polymer electrolyte. The fabrication method comprises a step of melting or dissolving in an organic solvent a polymer for forming a porous polymer matrix, a step of forming a porous polymer matrix by a spray method, and a step of injecting a polymer electrolyte solution into the obtained porous
20 polymer matrix.

The step of melting or dissolving a polymer for forming a porous polymer matrix is achieved by melting a polymer with heating, or by mixing a polymer in a suitable organic solvent and then stirring the mixture at a raised temperature, to obtain a clear polymeric solution. If a polymer is

dissolved in an organic solvent, the possible organic solvents used are not particularly limited on condition that they can dissolve the polymer substantially and be applicable to a spray method. In addition, a solvent which might influence on the characteristics of the battery can even be used,
5 because the solvent is almost completely removed while fabricating a porous polymer matrix by a spray method.

The step of forming a porous polymer matrix is achieved by a spray method. In more detail, the porous polymer matrix can be obtained by filling a polymeric melt or polymeric solution for forming a porous polymer matrix
10 into a barrel of a spray machine and then spraying the polymeric melt or polymeric solution onto a metal plate or Mylar film using a nozzle at a constant rate. In order to simplify the fabrication process, the polymeric melt or polymeric solution can be sprayed directly onto the electrode. A thickness of the porous polymer matrix can be adjusted by changing a spray speed and
15 time, and as described before, a preferable thickness range is 1 – 100 μm .

As illustrated in Figures 1a to 1c, when spraying the polymeric melt or polymeric solution using a nozzle, the polymeric melt or polymeric solution can be sprayed by electrostatic induction. Embodiments of spraying by electrostatic induction include the following methods. One method is that a
20 nozzle and an electrode are connected to be each given an electrical potential in order that the polymeric melt or polymeric solution coming out from the nozzle has an electrostatic charge (Figure 1a). Another method is that an additional electrode for electrostatic induction is located between a nozzle and an electrode in order to charge the polymeric melt or polymeric solution

sprayed through a nozzle (Figure 1b). Another method is to combine the above two methods (Figure 1c).

A variety of methods can be applied in fabricating a porous polymer separator film using a nozzle. Examples include a method of spraying polymeric melts or polymeric solutions all together, and another method of installing spraying nozzles separately, followed by spraying the respective polymeric melts or polymeric solutions sporadically and continually to form a multi-layered porous polymer matrix. Figures 2a and 2b illustrate the fabrication methods of a porous polymer matrix using a spray machine. Figure 2a illustrates the fabrication method by spraying all together using a nozzle to form a polymer matrix. Figure 2b illustrates the fabrication method by spraying sporadically and continually using separately installed nozzles to form a multi-layered polymer matrix.

A porous polymer matrix using two or more polymers can be obtained by the following methods. One method is by heating/melting or dissolving in an organic solvent two or more polymers, filling the obtained polymeric melt or solution into a barrel of a spray machine and then spraying the melt or solution using a nozzle, to fabricate a porous polymer separator film. Another method is by heating/melting or dissolving in an organic solvent two or more polymers respectively, filling the obtained melts or solutions into separate barrels of a spray machine and then spraying the respective melts or solutions using nozzles, to fabricate a porous polymer matrix.

The hybrid polymer electrolyte is obtained by injecting a polymer electrolyte solution into the porous polymer matrix fabricated by a spray

method. In more detail, after obtaining a polymer electrolyte solution by dissolving a polymer in a mixture of an organic electrolyte solution and a plasticizer, the obtained polymer electrolyte solution is injected into the porous polymer matrix by die-casting, to obtain the hybrid polymer electrolyte.

5 The examples of the organic electrolyte solution used for a polymer electrolyte solution can include propylene carbonate, butylene carbonate, 1,4-butyrolactone, diethyl carbonate, dimethyl carbonate, 1,2-dimethoxyethane, 1,3-dimethyl-2-imidazolidinone, dimethylsulfoxide, ethylene carbonate, ethylmethyl carbonate, N,N-dimethylformamide, N,N-dimethylacetamide, N-
10 methyl-2-pyrrolidone, polyethylenesulfonate, tetraethylene glycol dimethyl ether, acetone, alcohol or mixtures thereof. However, because the plasticizer can be removed while fabricating a battery, the kind of plasticizer is not particularly limited. The preferable weight ratio of a polymer, plasticizer and organic electrolyte solution used for a polymer electrolyte solution is in the
15 range of 1 : 1 – 20 : 1 - 20.

 The present invention also relates to a fabrication method for a lithium secondary battery comprising the above-described hybrid polymer electrolyte. Figures 3a to 3c illustrate the fabrication process in detail. Figure 3a illustrates a fabrication process for a battery, comprising inserting a hybrid polymer
20 electrolyte, which is prepared by incorporating a polymer electrolyte solution into a porous polymer matrix fabricated by a spray method, between an anode and a cathode, making the electrolytes and the electrodes into one body by a certain heat lamination process, inserting the resulting plate into a battery casing after laminating or rolling it, injecting an organic electrolyte solution into

the battery casing, and then finally sealing the casing. Figure 3b illustrates a fabrication process for a battery, comprising coating a hybrid polymer electrolyte onto both sides of a cathode or an anode, adhering an electrode having opposite polarity to the coated electrode onto the hybrid polymer electrolyte, making the electrolytes and the electrodes into one body by a certain heat lamination process, inserting the resulting plate into a battery casing after laminating or rolling it, injecting an organic electrolyte solution into the battery casing, and then finally sealing the battery casing. Figure 3c illustrates a fabrication process for a battery, comprising coating a hybrid polymer electrolyte onto both sides of one of two electrodes and onto one side of the other electrode respectively, adhering the electrodes closely together as the hybrid polymer electrolytes are faced to each other, making the electrolytes and the electrodes into one body by a certain heat lamination process, inserting the resulting plate into a battery casing after laminating or rolling it, injecting an organic electrolyte solution into the battery casing, and then finally sealing the battery casing.

The anode and cathode used for the lithium secondary battery are fabricated in the same way as in the conventional method, such as by mixing an appropriate amount of active materials, conducting materials and bonding agents with an organic solvent, casting the resulting mixture onto both sides of a copper or aluminum foil plate grid, and then drying and compressing all of them. An anode active material comprises one or more material selected from the group consisting of graphite, cokes, hard carbon, tin oxide and lithiated compounds thereof. A cathode active material is one or more material

selected from the group consisting of LiClO_2 , LiNiO_2 , LiNiCoO_2 , LiMn_2O_4 , V_2O_5 or V_6O_{13} . Metallic lithium or lithium alloys can also be used for an anode in the present invention.

5 Examples

The present invention will be described in more detail by way of the following examples, but those examples are given for the purpose to illustrate the present invention, not to limit the scope of it.

Example 1

10 1-1) Fabrication of a porous polymer matrix

20g of polyvinylidene fluoride (Kynar 761) was added to 100g of dimethylacetamide, and the resulting mixture was stirred at room temperature for 24 hours to give a clear polymeric solution. The obtained polymeric solution was filled into a barrel of a spray machine and sprayed onto a metal
15 plate at a constant rate using a nozzle, to fabricate a porous polymer matrix having a thickness of 50 μm .

1-2) Fabrication of a hybrid polymer electrolyte

To a mixture of 15g of 1M LiPF_6 solution in EC-DMC and 1g of DMA solution as a plasticizer, 0.5g of PAN (prepared by Polyscience Company,
20 molecular weight of about 150,000), 2g of polyvinylidene difluoride (Atochem Kynar 761) and 0.5g of PMMA (prepared by Polyscience Company) were added. The resulting mixture was blended for 12 hours and then heated at 130 °C for one hour to give a clear polymer electrolyte solution. When a viscosity of several thousands cps suitable for casting was obtained, the

polymeric electrolyte solution was cast onto the porous polymer matrix obtained in Example 1-1 by die-casting, to fabricate a hybrid polymer electrolyte in which the polymer electrolyte solution was incorporated into the porous polymer matrix.

5 1-3) Fabrication of a lithium secondary battery

The hybrid polymer electrolyte fabricated in Example 1-2 was inserted between a graphite anode and a LiCoO_2 cathode, and the resulting plates were cut so as to be 3 cm \times 4 cm in size and laminated. Terminals were welded on to the electrodes, and the laminated plate was inserted into a vacuum casing. A 1M LiPF_6 solution in EC-DMC was injected into the vacuum casing, and then the vacuum casing was vacuum-sealed to fabricate a lithium secondary battery.

Example 2

2-1) 20g of polyvinylidene fluoride (Kynar 761) was added to 100g of dimethylacetamide, and the resulting mixture was stirred at room temperature for 24 hours to give a clear polymeric solution. The obtained polymeric solution was filled into a barrel of a spray machine and sprayed onto both sides of a graphite anode at a constant rate using a nozzle, to fabricate a graphite anode coated with a porous polymer matrix film having a thickness of 50 μm .

2-2) To a mixture of 15g of 1M LiPF_6 solution in EC-DMC and 1g of DMA solution as a plasticizer, 0.5g of PAN (prepared by Polyscience Company, molecular weight of about 150,000), 2g of polyvinylidene difluoride (Atochem Kynar 761) and 0.5g of PMMA (prepared by Polyscience Company)

were added. The resulting mixture was blended for 12 hours and heated at 130 °C for one hour to give a clear polymer electrolyte solution. When a viscosity of several thousands cps suitable for casting was obtained, the polymer electrolyte solution was cast onto the porous polymer matrix obtained
5 in Example 2-1 by die-casting in order to generate a hybrid polymer electrolyte on both sides of a graphite anode.

2-3) A LiCoO_2 cathode was adhered onto the hybrid polymer electrolyte obtained in Example 2-2. The resulting plate was cut so as to be 3 cm × 4 cm in size and laminated. Terminals were welded on to the electrodes, and the
10 laminated plate was inserted into a vacuum casing. A 1M LiPF_6 solution in EC-DMC was injected into the vacuum casing, and then the casing was vacuum-sealed to fabricate a lithium secondary battery.

Example 3

3-1) 20g of polyvinylidene fluoride (Kynar 761) was added to 100g of
15 dimethylacetamide, and the mixture was stirred at room temperature for 24 hours to give a clear polymeric solution. The obtained polymeric solution was filled into a barrel of a spray machine and sprayed onto one side of a LiCoO_2 cathode at a constant rate using a nozzle, to fabricate a LiCoO_2 cathode coated with a porous polymer matrix film having a thickness of 50 μm on one
20 side of it.

3-2) To a mixture of 15g of 1M LiPF_6 solution in EC-DMC and 1g of DMA solution as a plasticizer, 0.5g of PAN (prepared by Polyscience Company, molecular weight of about 150,000), 2g of polyvinylidene difluoride (Atochem Kynar 761) and 0.5g of PMMA (prepared by Polyscience Company)

were added. The resulting mixture was blended for 12 hours and heated at 130°C for one hour to give a clear polymer electrolyte solution. When a viscosity of several thousands cps suitable for casting was obtained, the polymer electrolyte solution was cast onto the porous polymer matrix obtained in Example 3-1 by die-casting in order to generate a hybrid polymer electrolyte on one side of a LiCoO_2 cathode.

3-3) The LiCoO_2 cathode obtained in Example 3-2 was adhered onto both sides of the graphite anode obtained in Example 2-2 so as to face the hybrid polymer electrolytes to each other. The resulting plate was made into one body by heat lamination at 110°C, followed by cutting so as to be 3 cm × 4 cm in size and then laminated. Terminals were welded on to the electrodes, and then the laminated plate was inserted into a vacuum casing. A 1M LiPF_6 solution in EC-DMC was injected into the casing, and then the casing was vacuum-sealed to fabricate a lithium secondary battery.

Example 4

4-1) 10g of polyvinylidene fluoride (Kynar 761) and 10g of PAN (prepared by Polyscience Company, molecular weight of about 150,000) were added to 100g of dimethylacetamide, and the resulting mixture was stirred at 120°C for 24 hours to give a clear polymeric solution. The obtained polymeric solution was filled into a barrel of a spray machine and sprayed onto both sides of a graphite anode using a nozzle charged with 9kV at a constant rate, to fabricate a graphite anode coated with a porous polymer matrix film having a thickness of 50 μm .

4-2) To a mixture of 15g of 1M LiPF_6 solution in EC-DMC and 1g of

DMA solution as a plasticizer, 0.5g of PAN (prepared by Polyscience Company, molecular weight of about 150,000), 2g of polyvinylidenedifluoride (Atochem Kynar 761) and 0.5g of PMMA (prepared by Polyscience Company) were added. The resulting mixture was blended for 12 hours and heated at
5 130 °C for one hour to give a clear polymer electrolyte solution. When a viscosity of several thousands cps suitable for casting was obtained, the polymer electrolyte solution was cast onto the porous polymer matrix obtained in Example 4-1 by die-casting in order to generate a hybrid polymer electrolyte on both sides of a graphite anode.

10 4-3) The processes in Examples 4-1 and 4-2 were applied to one side of a LiCoO_2 cathode instead of to both sides of a graphite anode, to fabricate a LiCoO_2 cathode coated with a hybrid polymer electrolyte on one side of it.

4-4) The LiCoO_2 cathode obtained in Example 4-3 was adhered onto both sides of the graphite anode obtained in Example 4-2 so as to face the
15 hybrid polymer electrolytes to each other. The resulting plate was made into one body by heat lamination at 110°C, followed by cutting so as to be 3 cm × 4 cm in size and then laminated. Terminals were welded on to the electrodes, and then the laminated plate was inserted into a vacuum casing. A 1M LiPF_6 solution in EC-DMC was injected into the casing, and then the
20 casing was vacuum-sealed to fabricate a lithium secondary battery.

Example 5

5-1) Two polymeric solutions of 20g of polyvinylidene fluoride (Kynar 761) in 100g of dimethylacetamide and 20g of PAN (prepared by Polyscience Company, molecular weight of about 150,000) in 100g of dimethylacetamide

were filled into separate barrels of a spray machine respectively. And the two polymeric solutions were sprayed onto both sides of a graphite anode using different nozzles at a constant rate, to fabricate a graphite anode coated with a porous polymer matrix film having a thickness of 50 μm .

5 5-2) To a mixture of 15g of 1M LiPF_6 solution in EC-DMC and 1g of DMA solution as a plasticizer, 0.5g of PAN (prepared by Polyscience Company, molecular weight of about 150,000), 2g of polyvinylidenedifluoride (Atochem Kynar 761) and 0.5g of PMMA (prepared by Polyscience Company) were added. The resulting mixture was blended for 12 hours and heated at
10 130°C for one hour to give a clear polymer electrolyte solution. When a viscosity of several thousands cps suitable for casting was obtained, the polymer electrolyte solution was cast onto the porous polymer matrix obtained in Example 5-1 by die-casting in order to fabricate a graphite anode coated with a hybrid polymer electrolyte on both sides of it.

15 5-3) The processes in Examples 5-1 and 5-2 were applied to one side of a LiCoO_2 cathode instead of to both sides of a graphite anode, to fabricate a LiCoO_2 cathode coated with a hybrid polymer electrolyte on one side of it.

 5-4) The LiCoO_2 cathode obtained in Example 5-3 was adhered onto both sides of the graphite anode obtained in Example 5-2 so as to face the
20 hybrid polymer electrolytes to each other. The resulting plate was made into one body by heat lamination at 110°C, followed by cutting so as to be 3 cm \times 4 cm in size and then laminated. Terminals were welded on to the electrodes, and then the laminated plate was inserted into a vacuum casing. A 1M LiPF_6 solution in EC-DMC was injected into the casing, and then the

casing was vacuum-sealed to fabricate a lithium secondary battery.

Example 6

6-1) 20g of polyvinylidene fluoride (Kynar 761) was added to 100g of dimethylacetamide, and the mixture was stirred at room temperature for 24
5 hours to give a clear polymeric solution. The obtained polymeric solution was filled into a barrel of a spray machine and sprayed onto both sides of a graphite anode at a constant rate using a nozzle, to fabricate a graphite anode coated with a porous polymer matrix film having a thickness of 50 μm .

6-2) 2g of an oligomer of polyethylene glycol diacrylate (hereinafter
10 referred to as PEGDA, prepared by Aldrich Company, molecular weight of 742) and 3g of polyvinylidene difluoride (Atochem Kynar 761) were added to 20g of 1M LiPF_6 solution in EC-EMC. The resulting mixture was blended sufficiently enough to be homogenous at room temperature for 3 hours and then cast onto the porous polymer matrix obtained in Example 6-1. An
15 ultraviolet lamp having a power of 100W was irradiated onto the porous polymer matrix for about 1.5 hours in order to induce polymerization of the oligomer, to generate a polymer electrolyte on both sides of a graphite anode.

6-3) The processes in Examples 6-1 and 6-2 were applied to one side of a LiCoO_2 cathode instead of to both sides of a graphite anode, to fabricate
20 a LiCoO_2 cathode coated with a hybrid polymer electrolyte on one side of it.

6-4) The LiCoO_2 cathode obtained in Example 6-3 was adhered onto both sides of the graphite anode obtained in Example 6-2 so as to face the hybrid polymer electrolytes to each other. The resulting plate was made into one body by heat lamination at 110°C, followed by cutting so as to be 3 cm

× 4 cm in size and then laminated. Terminals were welded on to the electrodes, and then the laminated plate was inserted into a vacuum casing. A 1M LiPF₆ solution in EC-DMC was injected into the casing, and then the casing was vacuum-sealed to fabricate a lithium secondary battery.

5 Comparative Examples

Comparative example 1

A lithium secondary battery was fabricated by laminating electrodes and separator films in order of an anode, a PE separator film, a cathode, a PE separator film and an anode, inserting the resulting laminated plate into
10 a vacuum casing, injecting a 1M LiPF₆ solution in EC-DMC into the casing, and then finally vacuum-sealing the casing.

Comparative example 2

According to the conventional preparation method of a gel-polymer electrolyte, 9g of 1M LiPF₆ solution in EC-PC was added to 3g of PAN. The
15 resulting mixture was blended for 12 hours and then heated at 130°C for 1 hour to give a clear polymeric solution. When a viscosity of 10,000cps, suitable for casting was obtained, the polymeric solution was cast by die-casting to give a polymer electrolyte film. A lithium secondary battery was fabricated by laminating, in order, a graphite anode, an electrolyte, a LiCoO₂ cathode, an
20 electrolyte and a graphite anode, welding terminals onto the electrodes, inserting the laminated plate into a vacuum casing, injecting a 1M LiPF₆ solution in EC-DMC into the casing and then finally vacuum-sealing the casing.

Example 7

Charge/discharge characteristics of the lithium secondary batteries obtained in Examples 1 - 6 and Comparative Examples 1 and 2 were tested, and Figure 4 shows the results. The tests for obtaining the charge/discharge characteristics were performed by a charge/discharge method of, after
5 charging the batteries with a C/2 constant current and 4.2V constant voltage, discharging with a C/2 constant current, and the electrode capacities and cycle life based on the cathode were tested. Figure 4 shows that the electrode capacities and cycle life of the lithium secondary batteries of Examples 1 - 6 were improved compared to the lithium secondary batteries of Comparative
10 Examples 1 and 2.

Example 8

Low- and high-temperature characteristics of the lithium secondary batteries of Example 2 and Comparative Example 2 were tested, and Figures 5a and 5b illustrate the results (wherein Figure 5a is for Example 2 and Figure
15 5b is for Comparative Example 2). The tests for obtaining the low- and high-temperature characteristics of the lithium secondary batteries were performed by a charge/discharge method of, after charging the lithium batteries with a C/2 constant current and 4.2 V constant voltage, discharging with a C/5 constant current. Figures 5a and 5b show that the low- and high-temperature
20 characteristics of the lithium secondary battery of Example 2 are better than those of the battery of Comparative Example 2. In particular, it shows that the battery of Example 2 has an outstanding characteristic of 91% even at -10°C.

Example 9

High rate discharge characteristics of the lithium secondary batteries

of Example 2 and Comparative Example 2 were tested, and Figures 6a and 6b illustrate the results (wherein Figure 6a is for Example 2 and Figure 6b is for Comparative Example 2). The tests for obtaining the high rate discharge characteristics of the lithium secondary batteries were performed by a charge/discharge method of, after charging the lithium batteries with a C/2 constant current and 4.2 V constant voltage, discharging while varying the constant current to C/5, C/2, 1C and 2C. As depicted in Figures 6a and 6b, the lithium secondary battery of Example 2 exhibited capacities such as 99% at C/2 discharge, 96% at 1C discharge and 90% at 2C discharge based on the value of C/5 discharge. However, the lithium secondary battery of Comparative Example 2 exhibited low capacities such as 87% at 1C discharge and 56% at 2C discharge based on the value of C/5 discharge. Accordingly, it was discovered that the high rate discharge characteristic of the lithium secondary battery of Example 2 was better than that of the lithium secondary battery of Comparative Example 2.

CLAIMS

1. A hybrid polymer electrolyte comprising a porous polymer matrix in the form of particles or fibers, or a combination thereof having a diameter of 1-3000nm and an organic electrolyte solution dissolving a polymer and a lithium salt incorporated into the porous polymer matrix.
2. The hybrid polymer electrolyte according to claim 1, wherein the porous polymer matrix is fabricated by a spray method.
3. The hybrid polymer electrolyte according to claim 2, wherein the spray method is an electrostatic induction spray method.
4. The hybrid polymer electrolyte according to claim 1, wherein the porous polymer matrix has a thickness of 1 μm ~ 100 μm .
5. The hybrid polymer electrolyte according to claim 1, wherein the polymer for forming the porous polymer matrix is selected from the group consisting of polyethylene, polypropylene, cellulose, cellulose acetate, cellulose acetate butylate, cellulose acetate propionate, polyvinylpyrrolidone-vinylacetate, poly[bis(2-(2-methoxyethoxyethoxy))phosphagene], polyethyleneimide, polyethyleneoxide, polyethylenesuccinate, polyethylenesulfide, poly(oxymethylene-oligo-oxyethylene), polypropyleneoxide, polyvinyl acetate, polyacrylonitrile, poly(acrylonitrile-co-methylacrylate), polymethylmethacrylate, poly(methylmethacrylate-co-ethylacrylate), polyvinylchloride, poly(vinylidene-

chloride-co-acrylonitrile), polyvinylidenedifluoride, poly(vinylidene fluoride-co-hexafluoropropylene) and mixtures thereof.

6. The hybrid polymer electrolyte according to claim 1, wherein the
5 polymer incorporated into the porous polymer matrix is selected from the group consisting of polyethylene, polypropylene, cellulose, cellulose acetate, cellulose acetate butylate, cellulose acetate propionate, polyvinylpyrrolidone-vinylacetate, poly[bis(2-(2-methoxyethoxyethoxy))phosphagene], poly-ethyleneimide, polyethyleneoxide, polyethylenesuccinate, polyethylenesulfide,
10 poly(oxymethylene-oligo-oxyethylene), polypropyleneoxide, polyvinyl acetate, polyacrylonitrile, poly(acrylonitrile-co-methylacrylate), polymethylmethacrylate, poly(methylmethacrylate-co-ethylacrylate), polyvinylchloride, poly(vinylidene-chloride-co-acrylonitrile), polyvinylidenedifluoride, poly(vinylidene fluoride-co-hexafluoropropylene), polyethylene glycol diacrylate, polyethylene glycol
15 dimethacrylate or mixtures thereof.

7. The hybrid polymer electrolyte according to claim 1, wherein the lithium salt incorporated into the porous polymer matrix is LiPF_6 , LiClO_4 , LiAsF_6 , LiBF_4 or LiCF_3SO_3 .

20

8. The hybrid polymer electrolyte according to claim 1, wherein an organic solvent used in the organic electrolyte solution is ethylene carbonate, propylene carbonate, diethyl carbonate, dimethyl carbonate, ethylmethyl carbonate or mixtures thereof.

9. The hybrid polymer electrolyte according to claim 8, wherein the organic solvent further comprises methyl acetate, methyl propionate, ethyl acetate, ethyl propionate, butylene carbonate, γ -butyrolactone, 1,2-dimethoxyethane, 1,2-dimethoxyethane, dimethylacetamide, tetrahydrofuran
5 or mixtures thereof in order to improve a low-temperature characteristic.

10. The hybrid polymer electrolyte according to claim 1, wherein the hybrid polymer electrolyte further comprises a filling agent.

10

11. The hybrid polymer electrolyte according to claim 10, wherein the filling agent is selected from the group consisting of TiO_2 , BaTiO_3 , Li_2O , LiF , LiOH , Li_3N , BaO , Na_2O , MgO , Li_2CO_3 , LiAlO_2 , SiO_2 , Al_2O_3 , PTFE and mixtures thereof, and its content is not greater than 20wt% (excluding 0%) of the total
15 hybrid polymer electrolyte.

12. A fabrication method of a hybrid polymer electrolyte comprising:
a step of obtaining a polymeric solution by dissolving a polymer or a polymeric mixture in an organic solvent;
20 a step of filling the obtained polymeric solution into a barrel of a spray machine and then discharging the polymeric solution onto a substrate including a metal plate, a Mylar film and electrodes using a nozzle, to fabricate a porous polymer matrix; and

a step of injecting a polymer electrolyte solution in which a polymer is

dissolved in a mixture of a plasticizer and an organic electrolyte solution into the porous polymer matrix.

13. A fabrication method of a hybrid polymer electrolyte comprising:
- 5 a step of obtaining two or more polymeric solutions by dissolving two or more polymers in organic solvents respectively;
- a step of filling the obtained respective polymeric solutions into different barrels of a spray machine and then discharging the polymeric solutions onto a substrate including a metal plate, a Mylar film and electrodes
- 10 using different nozzles in order to fabricate porous polymer matrices; and
- a step of injecting a polymer electrolyte solution in which a polymer is dissolved in a mixture of a plasticizer and an organic electrolyte solution into the porous polymer matrices.
- 15 14. The fabrication method of a hybrid polymer electrolyte according to claim 12 or 13, wherein the plasticizer is selected from the group consisting of propylene carbonate, butylene carbonate, 1,4-butyrolactone, diethyl carbonate, dimethyl carbonate, 1,2-dimethoxyethane, 1,3-dimethyl-2-imidazolidinone, dimethylsulfoxide, ethylene carbonate, ethylmethyl
- 20 carbonate, N,N-dimethylformamide, N,N-dimethylacetamide, N-methyl-2-pyrrolidone, polyethylenesulfurane, tetraethylene glycol dimethyl ether, acetone, alcohol and mixtures thereof.

15. The fabrication method of a hybrid polymer electrolyte according to

claim 14, wherein the weight ratio of the polymer to the plasticizer included in the polymer electrolyte solution is 1 : 1 – 1 : 20, and the weight ratio of the polymer to the organic electrolyte solution is 1 : 1 – 1 : 20.

- 5 16. The fabrication method of a hybrid polymer electrolyte according to claim 15, wherein the polymer electrolyte solution is prepared by mixing the polymer, the plasticizer and the organic electrolyte solution, and then stirring the mixture at 20 – 150°C for 30 minutes - 24 hours to obtain a polymeric solution.

10

17. A lithium secondary battery comprising the hybrid polymer electrolyte according to claim 1.

18. A fabrication method of a lithium secondary battery, comprising
15 inserting the hybrid polymer electrolyte according to claim 1 between an anode and a cathode, inserting the resulting plates into a battery casing after laminating or rolling them, injecting an organic electrolyte solution into the battery casing, and sealing the casing.

- 20 19. A fabrication method of a lithium secondary battery, comprising:
inserting the hybrid polymer electrolyte according to claim 1 between an anode and a cathode;
making the electrolyte and electrodes into one body by a heat lamination process;

inserting the resulting plate into a battery casing after laminating or rolling it;

injecting an organic electrolyte solution into the battery casing; and sealing the casing.

5

20. A fabrication method of a lithium secondary battery, comprising:

coating the hybrid polymer electrolyte according to claim 1 onto both sides of a cathode or an anode;

adhering an electrode having opposite polarity to the coated electrode
10 onto the hybrid polymer electrolyte;

inserting the resulting plate into a battery casing after laminating or rolling it;

injecting an organic electrolyte solution into the battery casing; and sealing the battery casing.

15

21. A fabrication method of a lithium secondary battery, comprising:

coating the hybrid polymer electrolyte according to claim 1 onto both sides of a cathode or an anode;

adhering an electrode having opposite polarity to the coated electrode
20 onto the hybrid polymer electrolyte;

making the electrolytes and electrodes into one body by a heat lamination process;

inserting the resulting plate into a battery casing after laminating or rolling it;

injecting an organic electrolyte solution into the battery casing; and
sealing the battery casing.

22. A fabrication method of a lithium secondary battery, comprising:
5 coating the hybrid polymer electrolyte according to claim 1 onto both
sides of one of two electrodes and onto one side of the other electrode;
adhering the electrodes closely so as to face the hybrid polymer
electrolytes to each other;
inserting the resulting plate into a battery casing after laminating or
10 rolling it;
injecting an organic electrolyte solution into the battery casing; and
sealing the battery casing.
23. A fabrication method of a lithium secondary battery, comprising:
15 coating the hybrid polymer electrolyte according to claim 1 onto both
sides of one of two electrodes and onto one side of the other electrode;
adhering the electrodes closely so as to face the hybrid polymer
electrolytes to each other;
making the electrolytes and electrodes into one body by a certain
20 heat lamination process;
inserting the resulting plate into a battery casing after laminating or
rolling it;
injecting an organic electrolyte solution into the battery casing; and
sealing the battery casing.

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FIG.1A

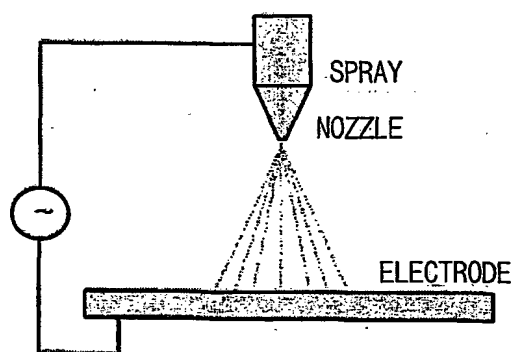


FIG.1B

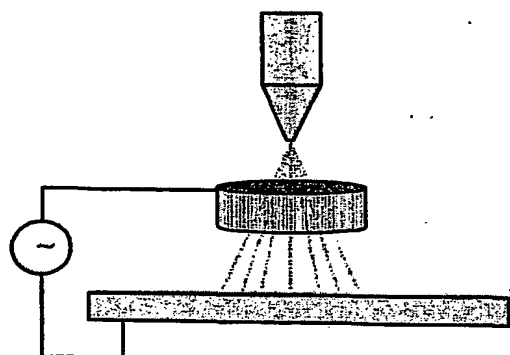
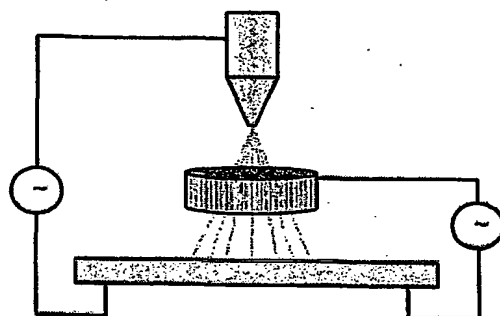


FIG.1C



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FIG. 2A

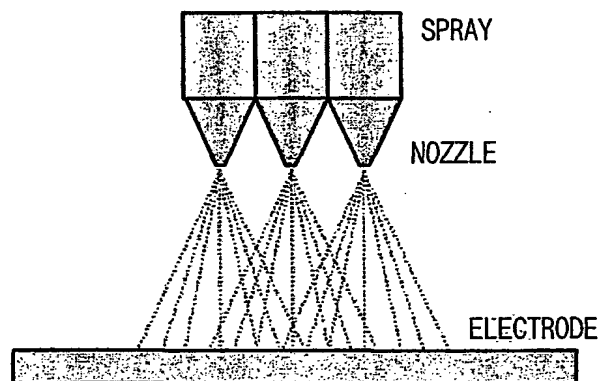
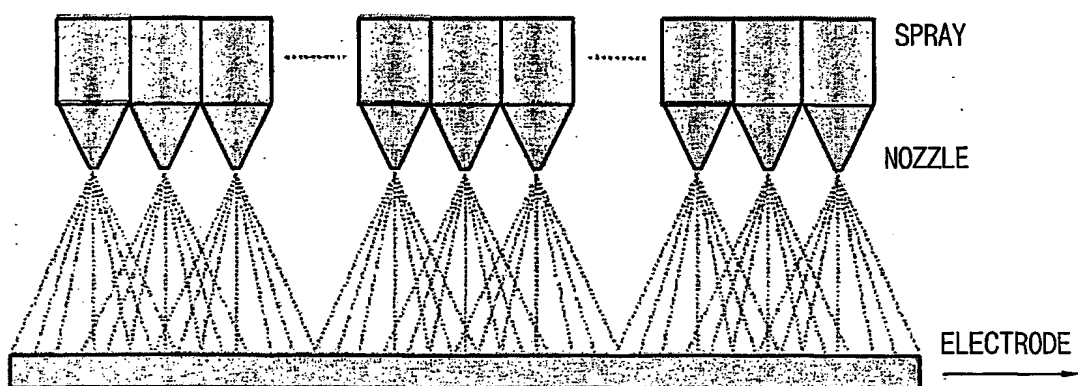


FIG. 2B



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FIG. 3A

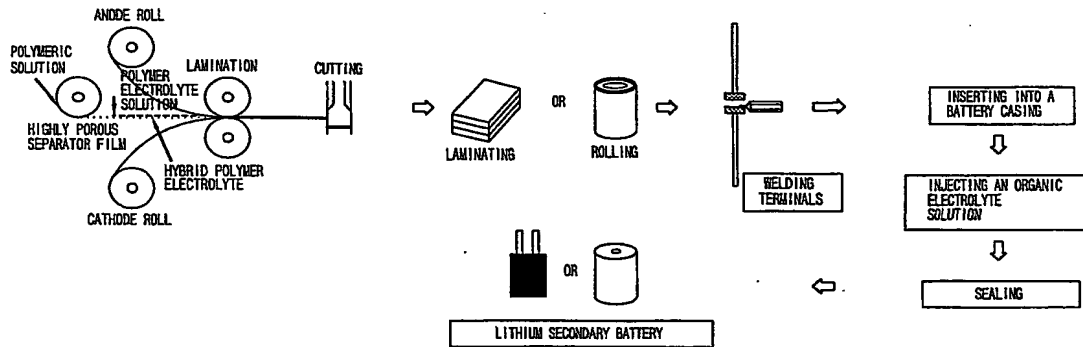


FIG. 3B

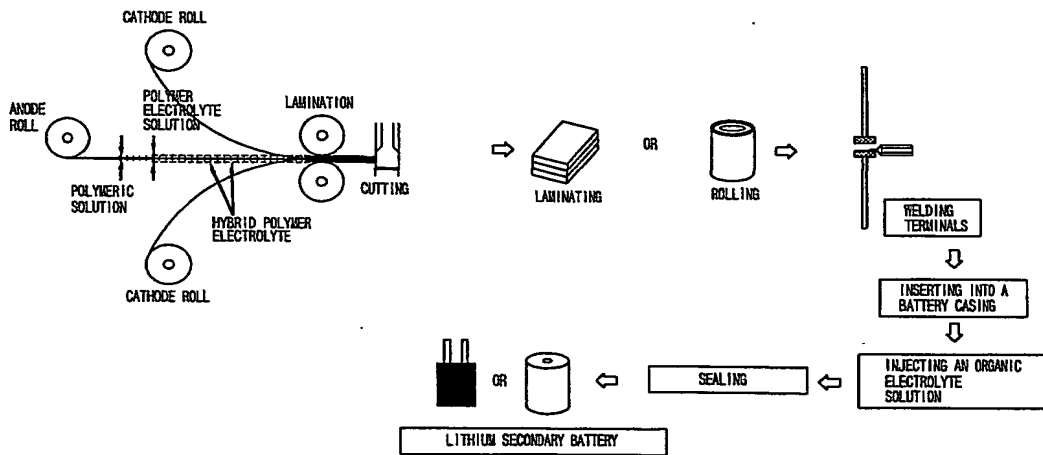
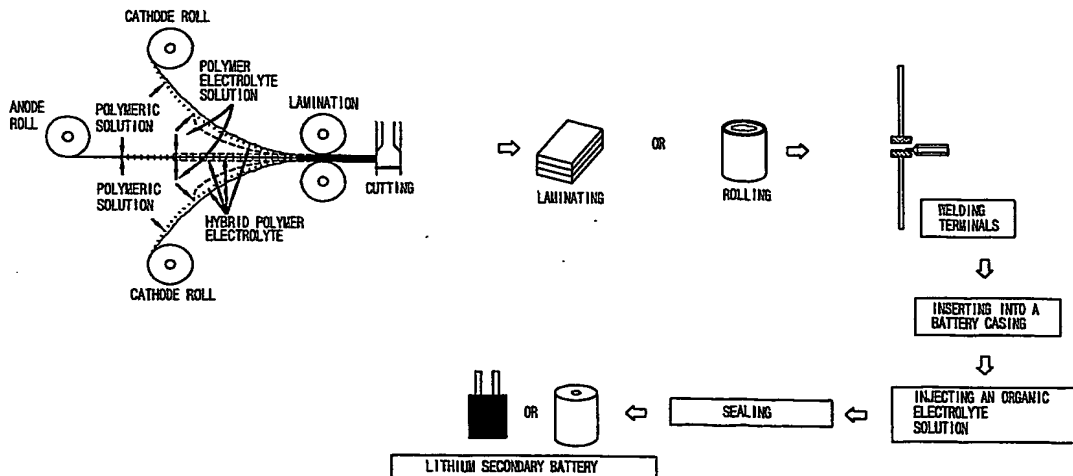
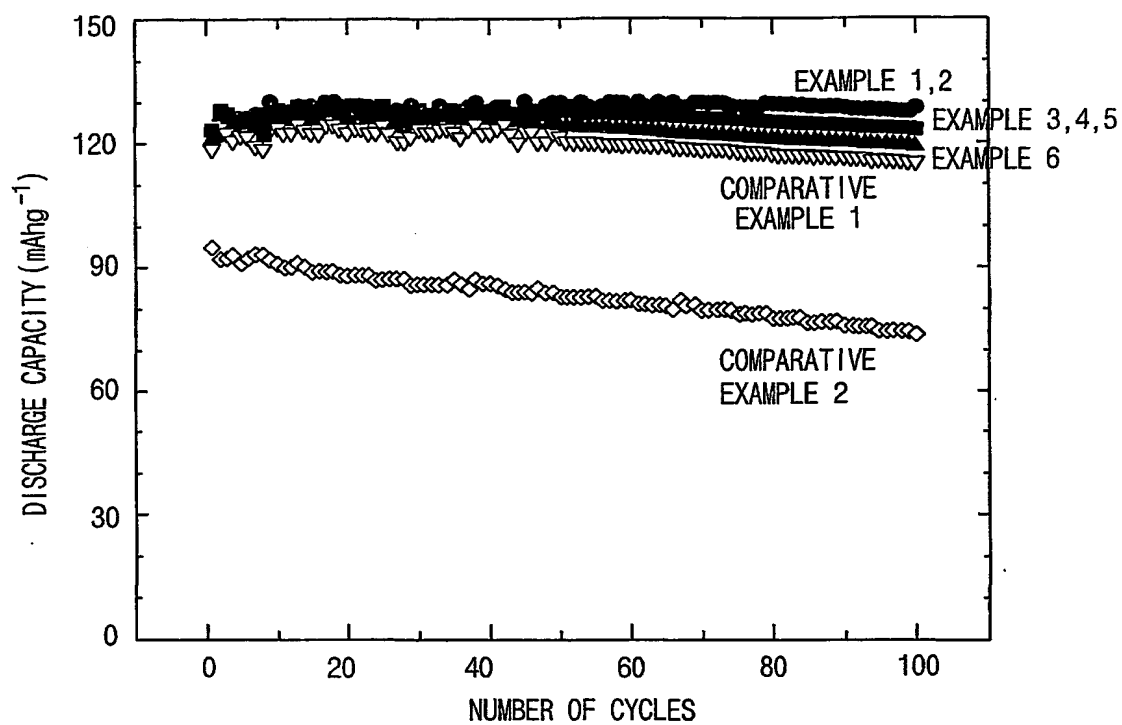


FIG. 3C



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FIG. 4



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FIG. 5A

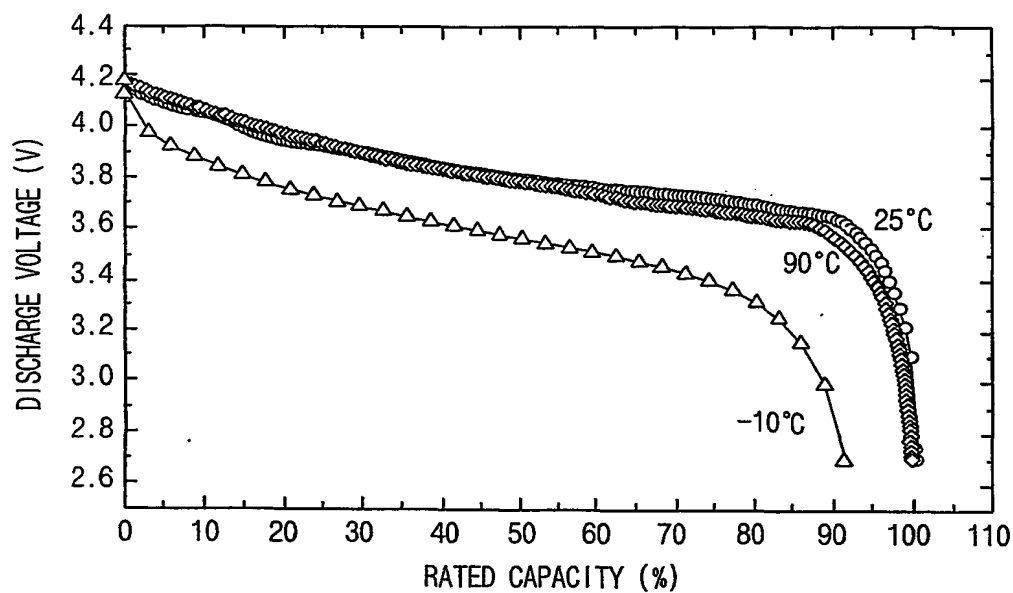
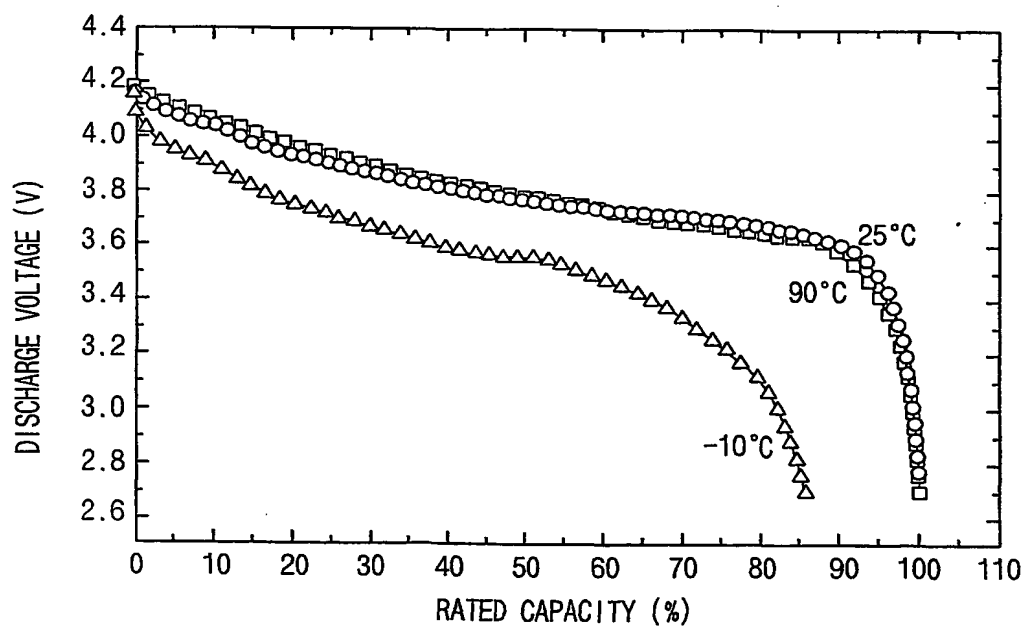


FIG. 5B



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FIG. 6A

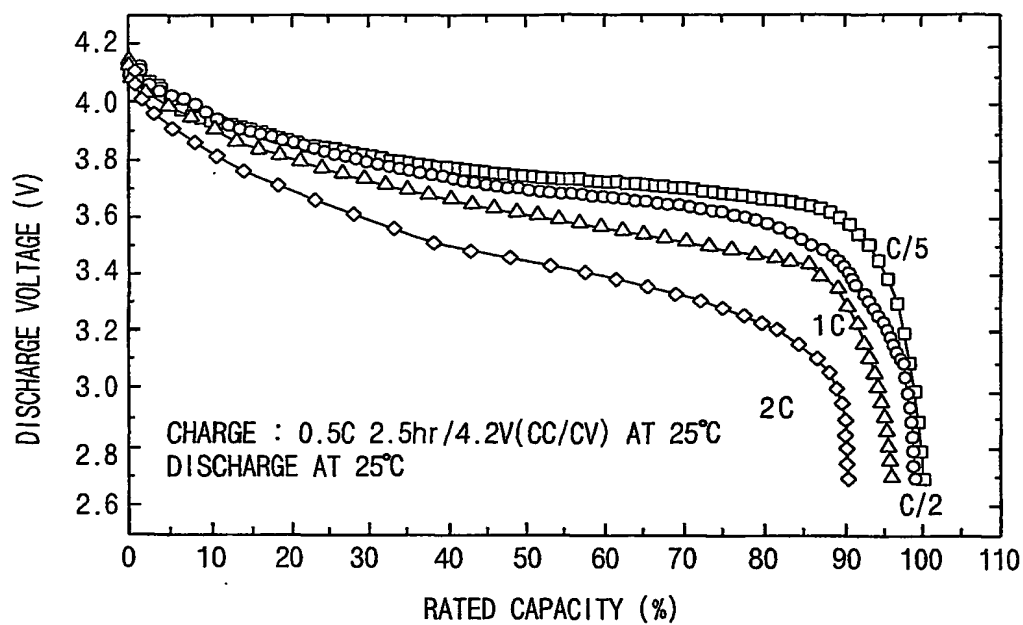
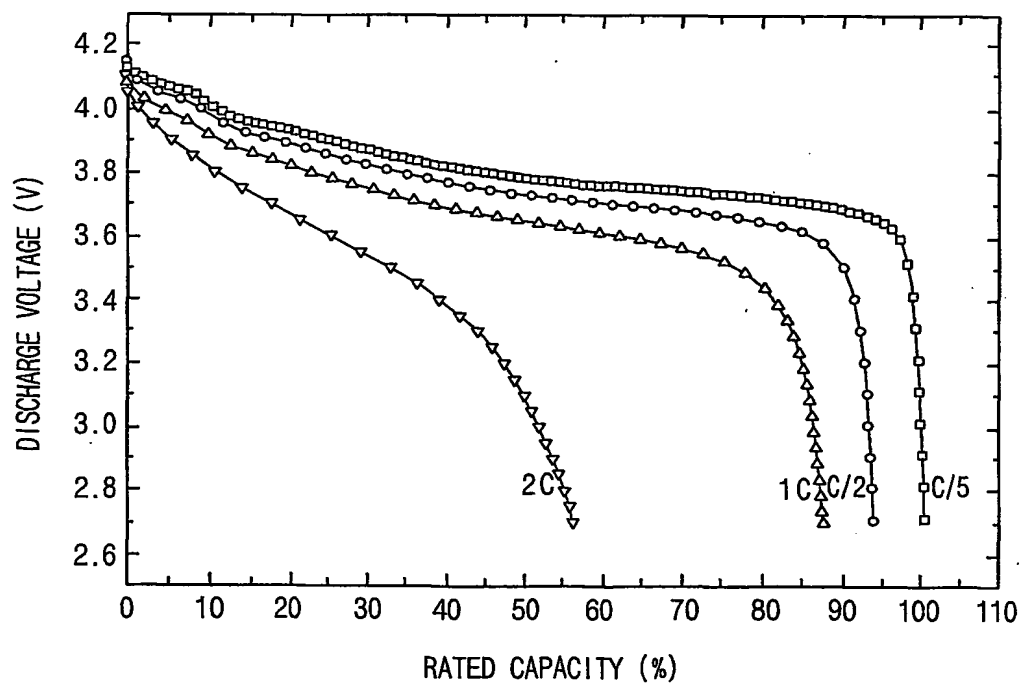


FIG. 6B



INTERNATIONAL SEARCH REPORT

International application No.

PCT/KR00/00513

A. CLASSIFICATION OF SUBJECT MATTER**IPC7 H01M 10/38**

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC7 : H01M; D01D; F02M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

USPAT, FPD, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	JP, B1, 08250100 (FUJI PHOTO FILM CO., LTD.) 27 SEPTEMBER 1996 SEE THE WHOLE DOCUMENT	1-11, 17
Y	US, A, 6051175 (POLYMER PROCESSING RESEARCH INST. LTD.) 18 APRIL 2000 SEE ABSTRACT	2-3, 12-16
Y	US, A, 3925525 (CELANESE CORPORATION) 9 DECEMBER 1975 SEE ABSTRACT, SEE CLAIM1	2-3, 12-16
Y	US, A, 5296185 (THE DOW JONES CHEMICAL COMPANY) 22 MARCH 1994 SEE THE WHOLE DOCUMENT	2-3, 12-16
Y	JP, A, 03038226 (ASAHI CHEM IND CO., LTD.) 19 FEBRUARY 1991 SEE THE WHOLE DOCUMENT	2-3, 12-16
Y	JP, A, 12082498 (NEC CORP.) 21 MARCH 2000 SEE THE WHOLE DOCUMENT	18-23
Y	US, A, 5525443 (MATSUSHITA ELECTRIC IND CO., LTD.) 11 JUNE 1996 SEE THE WHOLE DOCUMENT	8-9

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Date of the actual completion of the international search

28 FEBRUARY 2001 (28.02.2001)

Date of mailing of the international search report

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Authorized officer

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Telephone No. 82-42-481-5730



INTERNATIONAL SEARCH REPORT

International application No.

PCT/KR00/00513

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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Y	EP, A2, 0398689 (TOKYO SHIBAURA ELECTRIC CO. TOSHIBA BATTERY) 22 NOVEMBER 1990 SEE CLAIM4	7
Y	US, A, 4812375 (US ARMY,) 14 MARCH 1989 SEE THE WHOLE DOCUMENT	1, 17
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A	JP, A, 60252716 (MITSUBISHI RAYON CO., LTD.) 13 DECEMBER 1985 SEE THE CLAIM	1-11, 17

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